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The ground state energy of the Helium isoelectronic series

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Abstract A new approach to the evaluation of the ground state energy of the Helium isoelectronic series is presented here In this essentially perturbative approach, the screening parameter is fixed through the prescription of the vanishing of the first order correction This also makes the zero order energy variational The second order correction to the energy turns out to be constant for the whole series Results upto the second order are very encouraging

Keywords Ground state energy, Helium isoelectronic series, perturbative approach

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1. Introduction

The ground state (GS) of the helium atom, the simplest two electron system, has been well investigated using mainly the Ritz variational method with appropriate variational parameters to reflect the effects of the correlation and screening. Thus the one parameter variational wave function of Kellner [1] takes reasonably good account of the screening while the more extensive variational wavefunction (Hyllerass type [2]), using a large number of variational parameters, of Pekeris [3] gives a very accurate estimate of the GS energy. Somewhat earlier Chandrasekhar and Herzberg [4] with a few variational parameters obtained the GS energy remarkably close to the most accurate value. Subsequently many authors [5-9] with varying degrees of sophistication have reported reasonably good estimates of the GS energy (table 1). Similarly there have been some other calculations [10-18] which may briefly be called improvised variational approach giving very accurate GS energy. Despite these moderate to superior calculations the interest in the two electron systems remains unabated perhaps because of the challenging quest for even simpler and more transparent methods. It is in this spirit that we present in this communication a simple intuitive method which is a combination of an effective soluble hamiltonian and Rayleigh-Schrödinger Perturbation Theory (RSPT). The essence of the method, which leads to a good estimate of the GS energy, lies in a suitable partitioning of the exact hamiltonian into a soluble one (including the nuclear charge as a parameter) with a complete basis set and a

perturbation. As will be seen presently, the parameter in our effective hamiltonian is easily determined by a simple prescription which quite unpredictably makes our lowest order calculation variational ! We shall in the following sections describe in some detail our formulation of the problem leading finally to results and discussion. It will be seen that the novelty of the method is such that the whole isoelectronic series is covered by a single formalism and the calculations need be made for only one system to generate the results for the whole series.

2. Formulation

The hamiltonian for the two electron system in atomic units ($\hbar = m = e = 1$) is given by

$$\tilde{H} = -\frac{1}{2}\left(\nabla_{r_1}^2 + \nabla_{r_2}^2\right) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{|r_1 - r_2|}$$

$$= -\frac{1}{2}\left(\nabla_{r_1}^2 + \nabla_{r_2}^2\right) - Z'\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - (Z - Z')\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \tag{1}$$

where r_1, r_2 are the position coordinates of the electrons and Z, Z' are respectively the bare and effective ('screened') nuclear charges. For reasons to be apparent presently we introduce the following simple scaling

$$\rho = Z'r \quad \text{and} \quad H = \tilde{H} / Z' \tag{2}$$

with the result that

$$H = H_0 + H_I\,, \tag{3}$$

where

$$H_0 = -\frac{1}{2}\left(\nabla_{\rho_1}^2 + \nabla_{\rho_2}^2\right) - \left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) = \sum_{i=1}^{\tilde{}} h_{0i}\,, \tag{4}$$

$$h_{0i} = -\frac{1}{2}\nabla_{\rho_i}^2 - \frac{1}{\rho_i}\,, \tag{4.1}$$

and

$$H_I = \frac{1}{Z'}\left[-(Z - Z')\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{\rho_{12}}\right] \tag{5}$$

In this form, the spectrum of H_0, independent of Z or Z', is completely known as numbers in the discrete and the continuum. We shall estimate the ground state (GS) of H beginning from the GS of H_0 with H_I as perturbation. A general state of H_0, $\psi_{ij}(\rho_1, \rho_2)$ is given by

$$\psi_{ij}(\rho_1, \rho_2) = \begin{cases} \frac{1}{\sqrt{2}}\left[\varphi_i(\rho_1)\varphi_j(\rho_2) + \varphi_j(\rho_1)\varphi_i(\rho_2)\right] & i \neq j \\ \varphi_i(\rho_1)\varphi_j(\rho_2) & i = j \end{cases}, \tag{6}$$

where the φ's are single particle normalised hydrogenic wave functions in the appropriate states i or j. The states (6) are spin singlets which are all we shall need in the second order

perturbation of the GS of H_0, since the GS of H_0 is a spin singlet state and H_I is spin independent. The perturbation H_I has untill now an unknown parameter Z' which has to be determined. We fix this parameter by the prescription that the first order perturbation correction to the GS

$$< \psi_{gg}(\rho_1, \rho_2) \left| H_I \right| \psi_{gg}(\rho_1, \rho_2) > = 0 \tag{7}$$

with $$\psi_{gg}(\rho_1, \rho_2) = \varphi_g(\rho_1)\varphi_g(\rho_2) \text{ and } \varphi_g(\rho) = \pi^{-1/2} \exp(-1/\rho). \tag{7.1}$$

Eq. (7) reduces to

$$\frac{1}{Z'}\{-2(Z - Z') + 5/8\} = 0 \tag{8}$$

i.e. $(Z - Z') = 5/16$, a constant for the entire iso-electronic system. This has the important consequence that H_I given by equation (5) is proportional to $1/Z'$, the expression within the braces being independent of Z or Z'. It follows therefore that the perturbation series for the GS of H is given by

$$\begin{aligned} E_0 &= E_0^{gg} + E_1^{gg} + E_2^{gg} + \ldots\ldots\ldots \\ &= < \psi_{gg}(\rho_1, \rho_2) \left| H_0 \right| \psi_{gg}(\rho_1, \rho_2) > + < \psi_{gg}(\rho_1, \rho_2) \left| H_I \right| \psi_{gg}(\rho_1, \rho_2) > \\ &\quad - \sum{}' \frac{\left| < \psi_{gg}(\rho_1, \rho_2) \left| H_I \right| \psi_{ij}(\rho_1, \rho_2) > \right|^2}{E_0^{ij} - E_0^{gg}} + \ldots\ldots\ldots\ldots \\ &= a_0 + \frac{1}{Z'} a_1 + \frac{1}{Z'^2} a_2 + \ldots\ldots\ldots\ldots, \end{aligned} \tag{9}$$

where $a_0, a_1, a_2, a_3 \ldots\ldots$ are independent of Z or Z' and therefore need be calculated only once for the entire iso-electronic system. a_0 is trivially known and a_1 equals zero identically by our prescription which determines Z' as a function of Z. In the present communication we shall calculate the next order correction a_2, the details of which are analysed in the next section.

3. Results

a_2 is essentially the second order perturbation correction to the GS of H_0 and is given by

$$a_2 = -\sum_{i,j}{}' \frac{\left| < \psi_{gg}(\rho_1, \rho_2) \left| -\left(\frac{5}{16}\right)\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{\rho_{12}} \right| \psi_{ij}(\rho_1, \rho_2) > \right|^2}{E_0^{ij} - E_0^{gg}}, \tag{10}$$

where as usual the prime in the summation of (10) indicates that the intermediate state $\psi_{ij}(\rho_1, \rho_2) = \psi_{gg}(\rho_1, \rho_2)$ is excluded. $\psi_{gg}(\rho_1, \rho_2)$, the GS of H_0, is given explicitly by eq. (7.1).

The intermediate state $\psi_{ij}(\rho_1, \rho_2)$ of (10) are of three kinds, namely when (*i*) the

hydrogenic (ij) are both in the discrete spectrum, (ii) one of them in the discrete and other in the continuum (iii) both of them are in the continuum. Accordingly we classify the terms in the summation (10) as follows

1. Intermediate states discrete : $a_2^{dd} + a_2^{d\neq d'} + a_2^{dg} = A_2^{dd}$

$$a_2^{dd} \; [\, ij = dd,\, d \neq g\,;\, d \equiv (n, l, m),\, g \equiv (1,0,0)]$$

$$= -\sum_d{}' \frac{1}{E_0^{dd} - E_0^{gg}} < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| -\frac{5}{16}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\,\varphi_d(\rho_2) >< c.c >$$

$$= -\sum_d{}' \frac{1}{E_0^{dd} - E_0^{gg}} \left| < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\,\varphi_d(\rho_2) > \right|^2 \tag{11}$$

$$a_2^{d\neq d'} \; [\, ij = dd',\, d \neq d' \neq g\,;\, d \equiv (n_1, l_1, m_1),\, d' \equiv (n_2, l_2, m_2)]$$

$$= -\frac{1}{2} \sum_{\substack{d\neq d' \\ d'>d}}{}' \frac{1}{E_0^{dd'} - E_0^{gg}} < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| -\frac{5}{16}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\,\varphi_{d'}(\rho_2)$$

$$+ \varphi_d(\rho_2)\,\varphi_{d'}(\rho_1) >< c.c >$$

$$= -2 \sum_{\substack{d\neq d' \\ d'>d}}{}' \frac{1}{E_0^{dd'} - E_0^{gg}} \left| < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\,\varphi_{d'}(\rho_2) > \right|^2$$

$$= -\sum_{d\neq d'}{}' \frac{1}{E_0^{dd'} - E_0^{gg}} \left| < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\,\varphi_{d'}(\rho_2) > \right|^2 \tag{12}$$

$$a_2^{dd} + a_2^{d\neq d'} = -\sum_{d,d'}{}' \frac{1}{E_0^{dd'} - E_0^{gg}} \left| < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\,\varphi_{d'}(\rho_2) > \right|^2 \tag{13}$$

$$a_2^{dg} \; [\, ij = dg]$$

$$= -\frac{1}{2} \sum_d{}' \frac{1}{E_0^{dg} - E_0^{gg}} < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| -\frac{5}{16}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\,\varphi_g(\rho_2)$$

$$+ \varphi_d(\rho_2)\,\varphi_g(\rho_1) >< c.c >$$

$$= -\frac{1}{2} \sum_d{}' \frac{1}{E_0^{dg} - E_0^{gg}} < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| -\frac{5}{16}\frac{1}{\rho_1} + \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\,\varphi_g(\rho_2) >$$

$$+ < \varphi_g(\rho_1)\,\varphi_g(\rho_2) \left| -\frac{5}{16}\frac{1}{\rho_2} + \frac{1}{\rho_{12}} \right| \varphi_d(\rho_2)\,\varphi_g(\rho_1) >$$

$$= -\frac{1}{2}\sum_{d}{}' \frac{1}{E_0^{dg} - E_0^{gg}} \left| 2 < \varphi_g(\rho_1)\varphi_g(\rho_2) \left| -\frac{5}{16}\frac{1}{\rho_1} + \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\varphi_g(\rho_2) > \right|^2$$

$$= -2\sum_{d}{}' \frac{1}{E_0^{dg} - E_0^{gg}} \left| < \varphi_g(\rho_1)\varphi_g(\rho_2) \left| -\frac{5}{16}\frac{1}{\rho_1} + \frac{1}{\rho_{12}} \right| \varphi_d(\rho_1)\varphi_g(\rho_2) > \right| . \quad (14)$$

2. Intermediate states in discrete-continuum pairs : $a_2^{cd} + a_2^{cg} = A_2^{cd}$

a_2^{cd} [$ij = cd, d \neq g$; c denotes continuum]

$$= -\frac{1}{2}\sum_{cd} \frac{1}{E_0^{cd} - E_0^{gg}} < \varphi_g(\rho_1)\varphi_g(\rho_2) \left| -\frac{5}{16}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{\rho_{12}} \right| \varphi_c(\rho_1)\varphi_d(\rho_2)$$

$$+ \varphi_c(\rho_2)\varphi_d(\rho_1) >< c.c >$$

$$= -2\sum_{cd} \frac{1}{E_0^{cd} - E_0^{gg}} \left| < \varphi_g(\rho_1)\varphi_g(\rho_2) \right| \frac{1}{\rho_{12}} \left| \varphi_c(\rho_1)\varphi_d(\rho_2) > \right| \quad (15)$$

a_2^{cg} [$ij = cg$]

$$= -\frac{1}{2}\sum_{c} \frac{1}{E_0^{cg} - E_0^{gg}} < \varphi_g(\rho_1)\varphi_g(\rho_2) \left| -\frac{5}{16}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{\rho_{12}} \right| \varphi_c(\rho_1)\varphi_g(\rho_2)$$

$$+ \varphi_c(\rho_2)\varphi_g(\rho_1) >< c.c >$$

$$= -2\sum_{c} \frac{1}{E_0^{cg} - E_0^{gg}} \left| < \varphi_g(\rho_1)\varphi_g(\rho_2) \left| -\frac{5}{16}\frac{1}{\rho_1} + \frac{1}{\rho_{12}} \right| \varphi_c(\rho_1)\varphi_g(\rho_2) > \right|^2 . \quad (16)$$

3. Intermediate states both in continuum :

$a_2^{cc'} = A_2^{cc} \quad a_2^{cc'}$ [c' denotes continuum]

$$= -\frac{1}{2}\sum_{cc'} \frac{1}{E_0^{cc'} - E_0^{gg}} < \varphi_g(\rho_1)\varphi_g(\rho_2) \left| -\frac{5}{16}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) + \frac{1}{\rho_{12}} \right| \varphi_c(\rho_1)\varphi_{c'}(\rho_2)$$

$$+ \varphi_c(\rho_2)\varphi_{c'}(\rho_1) >< c.c >$$

$$= -\sum_{cc'} \frac{1}{E_0^{cc'} - E_0^{gg}} \left| < \varphi_g(\rho_1)\varphi_g(\rho_2) \right| \frac{1}{\rho_{12}} \left| \varphi_c(\rho_1)\varphi_{c'}(\rho_2) > \right|^2 . \quad (17)$$

In the derivation above from (11) to (17), the properties of orthogonality and symmetry have been used when appropriate. The basis set φ_{nlm} and φ_p employed for the discrete and continuum states of the hydrogenic system are given by

$$\varphi_{nlm}(\rho) = -N_{nl}\rho^l L_{n+l}^{2l+1}(2\gamma_n\rho)\, Y_{lm}(\hat{\rho}) , \quad (18)$$

where

$$N_{nl} = \frac{2}{n^2}\left(\frac{2}{n}\right)^l \left[\frac{(n-l-1)!}{\{(n+l)!\}^3}\right]^{1/2}$$

$$\gamma_n = 1/n .$$

$L_{n+l}^{2l+1}(2\gamma_n \rho)$ is the Laguere polynomial [19] and $Y_{lm}(\hat{\rho})$ is the spherical harmonic

and

$$\varphi_p(\rho) = N_p \exp(i\boldsymbol{p}\cdot\rho)\, F(i/p,1, ip\rho - i\boldsymbol{p}\cdot\rho), \tag{19}$$

where

$$N_p = \frac{}{(2\pi)^{3/2}} \exp(\pi/2p)\, \Gamma(1-i/p)$$

and $F(i/p,1,ip\rho - i\boldsymbol{p}.\rho)$ is the confluent hypergeometric function [20].

The wavefunctions satisfy the orthonormality relations

$$\int \varphi^*_{n'l'm'}(\rho)\varphi_{nlm}(\rho)d\rho = \delta_{nn'}\delta_{ll'}\delta_{mm'} \tag{20}$$

and

$$\int \varphi^*_{p'}(\rho)\varphi_p(\rho)d\rho = \delta(p-p'). \tag{21}$$

In our calculation, we have found it convenient to use the following contour integral representations of the Laguerre polynomial [21] and the confluent hypergeometric function [22]

$$L_{n+l}^{2l+1}(2\gamma_n\rho) = -\frac{(n+l)!}{2\pi i}\oint_c \frac{e^{-[2\gamma_n\{t/(1-t)\}\rho]}}{t^{n-l}(1-t)^{2l+2}}\,dt . \tag{22}$$

The contour c includes just the origin but excludes the other singularity at 1.

$$F(i/p,1, ip\rho - i\boldsymbol{p}.\rho)$$

$$= \left(\frac{1}{2\pi i}\right)\oint_\Gamma t^{-1+i/p}(t-1)^{-i/p} e^{t(p\rho - \boldsymbol{p}\cdot\rho)t}\,dt . \tag{23}$$

where Γ is the closed contour encircling the two points 0 and 1 once counterclockwise. There is a branch cut from 0 to 1 and the phases of t and $(t-1)$ are fixed by taking both of them as zero at the point where the contour crosses the real axis to the right of 1. The phase of each variable is measured from the positive real axis and it is positive when counterclockwise and negative when clockwise and can not exceed the value π.

The use of these contour integral representations have considerably faciliated the evaluation of various matrix elements by residue calculation.

The matrix elements that are required for the evaluation of (10) are classified in eq. (11) to (17) in simple sequential forms for easy computer adaptation. The typical matrix elements are

those of $1/\rho$ and $1/\rho_{12}$ the latter being somewhat difficult to handle analytically. We briefly present here the calculation of the relevant matrix elements (required for computer adaptation) with explanation of the symbols used.

a. $$I_1 = <\varphi_{100}(\rho)\left|\frac{1}{\rho}\right|\varphi_{nlm}(\rho)>$$

Substituting the integral representation (22) for the Laguerre Polynomial we carry out the space integration to obtain

$$I_1 = \delta_{l,0}\delta_{m,0}N_{nl}N_{10}(n+l)!\frac{1}{2\pi i}\oint\frac{dt}{t^n[(\gamma_n+\gamma_1)^2-(\gamma_1-\gamma_n)t]^2}.$$

Now after the calculation of the residue at $t=0$, we finally have the result

$$I_1 = 4n^{-3/2}\delta_{l,0}\delta_{m,0}\frac{(1-1/n)^{n-1}}{(1+1/n)^{n+1}}.$$

b. $$I_2 = <\varphi_{100}(\rho_1)\varphi_{100}(\rho_2)\left|\frac{1}{\rho_{12}}\right|\varphi_{n_1l_1m_1}(\rho_1)\varphi_{n_2l_2m_2}(\rho_2)>$$

Substituting $\varphi_{nlm}(\rho)$ from (18) and using

$$\frac{1}{\rho_{12}} = \frac{4\pi}{2l+1}\sum\frac{\rho_<^l}{\rho_>^{l+1}}Y_{lm}^*(\hat{\rho}_1)Y_{lm}(\hat{\rho}_2),$$

we carry out integration to obtain

$$I_2 = S(2l+2)!\{J_1+J_2+J_3\},$$

where $$S = \delta_{l_1,l}\,\delta_{l_2,l}\,\delta_{m_1,m}\,\delta_{m_2,-m}\frac{4}{2l+1}N_{n_1l_1}N_{n_2l_2},$$

$$J_1 = \left(\frac{1}{2\pi i}\right)^2\oint\oint\frac{(1-t_1)^3(1-t_2)\,dt_1dt_2}{t_1^N t_2^M(b_1-c_1t_1)^2(A-X_1t_1-X_2t_2+Bt_1t_2)^{2l+3}},$$

$$J_2 = \left(\frac{1}{2\pi i}\right)^2\oint\oint\frac{(1-t_2)^3(1-t_1)\,dt_1dt_2}{t_1^N t_2^M(b_2-c_2t_2)^2(A-X_1t_1-X_2t_2+Bt_1t_2)^{2l+3}},$$

$$J_3 = \left(\frac{1}{2\pi i}\right)^2\oint\oint\frac{(1-t_2)^2(1-t_1)^2\,dt_1dt_2}{t_1^N t_2^M(b_1-c_1t_1)(b_2-c_2t_2)(A-X_1t_1-X_2t_2+Bt_1t_2)^{2l+3}},$$

$$b_1 = 1+1/n_1,$$

$$c_1 = 1-1/n_1,$$

$$b_2 = 1 + 1/n_2 ,$$

$$c_2 = 1 - 1/n_2 ,$$

$$A = b_1 + b_2 ,$$

$$B = c_1 + c_2 ,$$

$$X_1 = b_1 + c_2 ,$$

$$X_2 = b_2 + c_1 .$$

To evaluate J_1, J_2, J_3, the contour integration with respect to t_2 is done by finding out the residue at $t_2 = 0$ and we have

$$J_1 = \left[J_{MN} - 3J_{M(N-1)} + 3J_{M(N-2)} - J_{M(N-3)}\right] \frac{[2l+3]_{M-1}}{(M-1)!}$$

$$- \left[J_{(M-1)N} - 3J_{(M-1)(N-1)} + 3J_{(M-1)(N-2)} - J_{(M-1)(N-3)}\right] \frac{[2l+3]_{M-2}}{(M-2)!} ,$$

$$J_2 = \left[J'_{NM} - 3J'_{N(M-1)} + 3J'_{N(M-2)} - J'_{N(M-3)}\right] \frac{[2l+3]_{N-1}}{(N-1)!}$$

$$- \left[J'_{(N-1)M} - 3J'_{(N-1)(M-1)} + 3J'_{(N-1)(M-2)} - J'_{(N-1)(M-3)}\right] \frac{[2l+3]_{N-2}}{(N-2)!}$$

and

$$J_3 = b_2^{-1}\left[\{K_{MN} - 2K_{M(N-1)} + K_{M(N-2)}\} - 2\{K_{(M-1)N} - 2K_{(M-1)(N-1)} + K_{(M-1)(N-2)}\} + \{K_{(M-2)N} - 2K_{(M-2)(N-1)} + K_{(M-2)(N-2)}\}\right],$$

where

$$J_{MN} = \left(\frac{1}{2\pi i}\right) \oint \frac{(X_2 - Bt_1)^{M-1} dt_1}{t_1^N (b_1 - c_1 t_1)^2 (A - X_1 t_1)^{2l+M+2}} ,$$

$$J'_{NM} = \left(\frac{1}{2\pi i}\right) \oint \frac{(X_1 - Bt_2)^{N-1} dt_2}{t_2^N (b_2 - c_2 t_2)^2 (A - X_2 t_2)^{2l+N+2}}$$

and

$$K_{MN} = \sum_{p=0}^{M-1} \frac{[2l+3]_p}{p!} \left(\frac{c_2}{b_2}\right)^{M-1-p}$$

$$\left(\frac{1}{2\pi i}\right) \oint \frac{(X_2 - Bt_1)^p dt_2}{t_1^N (b_1 - c_1 t_1)^2 (A - X_1 t_1)^{2l+3+p}} .$$

These are evaluated by calculating the residue at $t_1 = 0$. Thus

$$J_{MN} = \sum_{p=0}^{(M-1) \text{ or } (N-1), \text{ whichever is small}} X_2^{M-1} \frac{[-(M-1)]_p}{p!} \left(\frac{B}{X_2}\right)^p \sum_{q=0}^{N-1-p} A^{-(2l+M+2)}$$

$$\times \frac{[2l+M+2]_q}{q!} \left(\frac{X_1}{A}\right)^q (N-p-q)\, b_1^{-2} \left(\frac{c_1}{b_1}\right)^{N-1-p-q},$$

$$J'_{NM} = \sum_{p=0}^{(M-1) \text{ or } (N-1), \text{ whichever is small}} X_1^{N-1} \frac{[-(N-1)]_p}{p!} \left(\frac{B}{X_1}\right)^p \sum_{q=0}^{M-1-p} A^{-(2l+N+2)}$$

$$\times \frac{[2l+N+2]_q}{q!} \left(\frac{X_2}{A}\right)^q (M-p-q)\, b_2^{-2} \left(\frac{c_2}{b_2}\right)^{M-1-p-q}$$

and

$$K_{MN} = \sum_{p=0}^{M-1} \frac{[2l+3]_p}{p!} \left(\frac{c_2}{b_2}\right)^{M-1-p} X_2^p\, A^{-(2l+3+p)} b_1^{-1}$$

$$\times \sum_{r=0}^{p \text{ or } (N-1), \text{ whichever is small}} \frac{[-p]_r}{r!} \left(\frac{B}{X_2}\right)^r \sum_{q=0}^{N-1-r} \frac{[2l+p+3]_q}{q!} \left(\frac{X_1}{A}\right)^q \left(\frac{c_1}{b_1}\right)^{N-1-r-q}$$

c. $$I_3 = \langle \varphi_{100}(\rho) \left| \frac{1}{\rho} \right| \varphi_p(\rho) \rangle$$

Making use of integral representation of the confluent hypergeometric function (23) we get

$$I_3 = N_{10} N_p \left(\frac{1}{2\pi i}\right) \int\int \oint \frac{e^{-\mu\rho}}{\rho} e^{i\kappa\rho}\, t^{-1+i\alpha} (t-1)^{-i\alpha}\, d\rho\, dt,$$

where

$$\mu = 1 - ipt \text{ and } \kappa = \dot{p}(1-t).$$

Carrying out the space integration we get

$$I_3 = N_{10} N_p \frac{4\pi}{2\pi i} \oint \frac{1}{(\kappa^2 + \mu^2)} t^{-1+i\alpha} (t-1)^{-i\alpha}\, dt$$

with

$$\kappa^2 + \mu^2 = p^2(1-t^2)+(1-ipt)^2$$

$$= -2p\,(p+i)\,(t-t_0)$$

and

$$t_0 = \frac{(p^2+1)}{2p(p+i)}\,.$$

In view of the fact that the integral over the circle of infinite radius $|\,t\,| \to \infty$ vanishes, we can easily evaluate this integral by calculation of the residue at $t = t_0$ and we have

$$I_3 = \frac{2\pi}{p(p+i)} N_{10} N_p t_0^{-1+i\alpha}\,(t_0-1)^{-i\alpha}\,.$$

d. $$I_4 = <\varphi_{100}(\rho_1)\,\varphi_{100}(\rho_2) \qquad \varphi_{nlm}(\rho_1)\varphi_p(\rho_2)>$$

Now using the result

$$\frac{1}{\rho_{12}} = \frac{1}{2\pi^2}\int \frac{\exp\{iq.(\rho_1-\rho_2)\}}{} dq\,,$$

we have

$$I_4 = \frac{1}{2\pi^2}\int \frac{\varphi_1(q)\,\varphi_2(-q)}{q^2}\,dq\,,$$

where $$\varphi_1(q) = \int \varphi_{100}(\rho_1)\varphi^*_{nlm}(\rho_2)\exp(iq.\rho_1)\,d\rho_1$$

$$\frac{N_{10}N_{nl}}{2\sqrt{\pi}}(n+l)!\,4\pi\,(-i)^l 2^l l!\,q^l Y^*_{lm}(\hat{q})\,(-\frac{\upsilon}{\partial\gamma_1})J\,,$$

$$= \left(\frac{1}{2\pi i}\right)\oint \frac{dt}{t^{n-l}(1-t)^{2l+2}\,(q^2+\lambda^2)^{l+1}}\,,$$

$$\lambda = (\gamma_1+\gamma_n)+\frac{2\gamma_n t}{1-t}$$

$$= \frac{R-Ut}{1-t}\,,$$

$$R = \gamma_1+\gamma_n\,,$$

$$U = \gamma_1-\gamma_n\,,$$

and $$\varphi_2(-q) = \int \varphi_{100}(\rho_1)\varphi_p^*(\rho_2)\exp(-iq.\rho_2)\,d\rho_2$$

$$= \frac{N_{10}N_p}{2\sqrt{\pi}}\left(-\frac{\partial}{\partial\gamma_1}\right)\frac{1}{2\pi i}\frac{(2\pi)^3}{2\pi^2}\oint\frac{1}{(p'^2+\gamma_1'^2)}t^{-1+i\alpha}(t-1)^{-i\alpha}\,dt,$$

where

$$\gamma_1' = \gamma_1 - ipt,$$

$$p' = p(1-t) - q.$$

Now writing $p'^2 + \gamma_1'^2 = a' - b't$,

where

$$a' = p^2 + q^2 + \gamma_1^2 - 2q.p,$$

$$b' = 2p^2 + 2i\gamma_1 p - 2q.p,$$

the contour integration can be performed and we get

$$\varphi_2(-q) = 2\sqrt{\pi}N_{10}N_p\left(\frac{\partial}{\partial\gamma_1}\right)[a'^{-1+i\alpha}(a'-b')^{-i\alpha}].$$

On using the result [23],

$$\int \exp(-\lambda r)\,r^{l-1}\,Y_{lm}(\hat{r})\exp(ik.r)\,dr$$

$$\frac{4\pi(2i)^l l!\,k^l Y_{lm}(\hat{k})}{(k^2+\lambda^2)^{l+1}}$$

and writing

$$q^2 + \lambda^2 = q^2 + \frac{[R-Ut]^2}{1-t}$$

$$-\frac{\xi - 2wt - st^2}{(1-t)^2}$$

where

$$\xi = q^2 + (\gamma_1 + \gamma_n)^2,$$

$$w = q^2 + (\gamma_1^2 - \gamma_n^2),$$

$$s = q^2 + (\gamma_1 - \gamma_n)^2,$$

we get

$$\varphi_1(q) = C' q^l Y^*_{lm}(\hat{q}) \left(-\frac{\partial}{\partial \gamma_1}\right)\left(\frac{1}{2\pi i}\right)\frac{1}{\xi^{l+1}} \oint \frac{dt}{t^{n-l}(1-2x\beta_1-\beta_1^2)^{l+1}}$$

$$= C' q^l Y^*_{lm}(\hat{q}) \left(-\frac{\partial}{\partial \gamma_1}\right)\left[\frac{1}{\xi^{l+1}} C^{l+1}_{n-l-1}(w/\sqrt{\xi s})\,(\sqrt{s}/\xi)^{n-l-1}\right],$$

where

$$C' = \frac{N_{10} N_{nl}}{2\sqrt{\pi}} (n+l)!\, 4\pi (-i)^l 2^l l!,$$

$$x = w/\xi s,$$

$$\beta_1 = (\sqrt{s}/\xi) t.$$

Thus

$$I_4 = \frac{1}{2\pi^2} C'(-2\sqrt{\pi} N_{10} N_P) \int q^l Y^*_{lm}(\hat{q}) \left(\frac{\partial J}{\partial \gamma_1}\right)\Big[(i\alpha-1)\, a'^{i\alpha-2}$$

$$(a'-b')^{-i\alpha}\, 2\gamma_1 - i\alpha\,(a'-b')^{-i\alpha-1}\, a'^{i\alpha-1}\, 2(\gamma_1 - ip)\Big] dq$$

$$= \frac{1}{2\pi^2} C'(-2\sqrt{\pi} N_{10} N_P) \int dq\, q^l \left(\frac{\partial J}{\partial \gamma_1}\right)\Big[(i\alpha-1)(a'-b')^{-i\alpha}\, 2\gamma_1 I_1(q)$$

$$-i\alpha\,(a'-b')^{-i\alpha-1}\, 2(\gamma_1 - ip)\, I_2(q)\Big],$$

where

$$I_1(q) = \int a'^{i\alpha-2} Y^*_{lm}(\hat{q}) d\Omega_q$$

$$= \int \{p^2 + q^2 + \gamma_1^2 - 2q.p\}^{i\alpha-2} Y^*_{lm}(\hat{q}) d\Omega_q$$

$$= \frac{\pi\, Y^*_{lm}(\hat{p})}{pq(i\alpha+3)} \Big[\{(p+q)^2 + \gamma_1^2\}^{i\alpha-1}$$

$$\times\ {}_2F_1\left(-l, l+1, i\alpha; \frac{p^2+q^2+\gamma_1^2+2qp}{4pq}\right) + (-1)^{l+1}$$

$$\times \{(p-q)^2 + \gamma_1^2\}^{i\alpha-1}\ {}_2F_1\left(-l, l+1, i\alpha; \frac{2qp-(p^2+q^2+\gamma_1^2)}{4pq}\right)$$

and

$$I_2(q) = \int a'^{i\alpha-1} Y_{lm}^*(\hat{q}) d\Omega_q$$

is obtained from $I_1(q)$ [25] just by replacing $i\alpha$ by $(i\alpha + 1)$.

e. $$I_5 = <\varphi_{100}(\rho_1)\varphi_{100}(\rho_2)\left|\frac{1}{\rho_{12}}\right|\varphi_{p_1}(\rho_1)\varphi_{p_2}(\rho_2)>$$

Making use of the contour integral representation of the continuum wave functions $\varphi_{p_1}, \varphi_{p_2}$ [eq. (23)] we can write

$$I_5 = C''\left(\frac{1}{2\pi i}\right)^2 \iint\oint\oint \frac{e^{-(\mu_1\rho_1+\mu_2\rho_2)}}{\rho_{12}} \exp(i\chi_1\cdot\rho_1)\exp(i\chi_2\cdot\rho_2)$$

$$\times t_1^{-1+i\alpha_1}(t_1-1)^{-i\alpha_1} t_2^{-1+i\alpha_2}(t_2-1)^{-i\alpha_2} dt_1 dt_2 d\rho_1 d\rho_2,$$

where

$$C'' = \frac{1}{\pi}\frac{1}{(2\pi)^3}\exp(\pi/2p_1)\Gamma(1-i/p_1)\exp(\pi/2p_2)\Gamma(1-i/p_2),$$

$$\alpha_i = \frac{1}{p_i},$$

$$\mu_1 = \gamma_0 - ip_1 t_2,$$

$$\mu_2 = \gamma_0' - ip_2 t_2,$$

$$\chi_i = p_i(1-t_i).$$

Using the results

$$\frac{e^{-\mu_i\rho_i}}{\rho_i} = \frac{1}{2\pi^2}\int \frac{e^{iq_i\cdot\rho_i}}{(q_i^2+\mu_i^2)} dq_i$$

and

$$\frac{1}{\rho_{12}} = \frac{1}{2\pi^2}\int \frac{e^{iq_3(\rho_1-\rho_2)}}{q_3^2} dq_3,$$

the space integration can be carried out with the help of the two resulting delta functions the integrations with respect to q_1 and q_2 also can be done.

$$a_2 = A_2^{dd} + A_2^{cd} + A_2^{cc} = -0.0518\,.$$

The value is sufficiently accurate up to the quoted figure.

The discrete summation for the discrete states and the integration for the continuum states appearing in the second order perturbation are performed numerically by computer. For the numerical integration convergence has been tested so that the result should be accurate up to the sixth significant figure and the discrete summation is also cut off ensuring that there is no further contribution in the sixth significant figure.

Therefore the GS energy of the Helium isoelectronic series upto second order RSPT is given by

$$E = E_0 Z'^2 = a_0 Z'^2 + a_1 Z' + a_2\,,$$

$$= -Z'^2 + 0 - 0.0518\,,$$

$$= -(Z - 5/16)^2 - 0.0518\,.$$

In Table 1, we present our result together with some selective set of result as often quoted in the literature.

Table 1.

Z =	Freund *et al* [17]	One parameter variational result	Two parameter result of abbot and Maslen [7]	Three parameter result of Wu [8]	Two parameter result of tripathi *et al* [9]	Presernt Work
1.	0.5275	0.47266	0.508	0.5213	0.50552	0.52447
2	2 90372	2.84766	2.890	2.8994	2.88403	2 89947
3	7 27991	7.22266	7.267	7 2757	7 25990	7 27447
4	13.65556	13.59766	13.65	13.6513	13 63527	13 64947
5.	22.03097	21 97266	22 02		22.01048	22.02447
6.	32 40624	32.34766	32 39		32.38562	32.39947
7.	44.78144	44.72266	44.76		44.76071	44.77447
8	59.15659	59.09766			59.13578	59.14947
9.	75.53171	75.47266			75.51083	75.52447
10	93.90680	93.84766			93 88587	93.89947

4. Discussion

The results obtained for the helium isoelectronic series by the present method are quite interesting. The method essentially is a perturbative one with the effective zero order hamiltonian chosen in such a way that screening is included in the zeroth order hamiltonian through an effective charge Z'. By a simple scaling, the exact hamiltonian is recast in such a way that the zero order effective hamiltonian gives a known spectrum of numbers (in the discrete as well as in the continuum) and the perturbation becomes proportional to $f(\rho_1, \rho_2, \rho_{12}, Z-Z')/Z'$, where

f is essentially a function of ρ_1, ρ_2 and ρ_{12} since the contribution $Z - Z'$ turns out to be a constant ($\equiv 5/16$) for the whole iso-electronic system. Thus the scaled energy is just a series in $1/Z'$,

$$E/Z'^2 = \varepsilon = a_0 + a_1/Z' + a_2/Z'^2 + -a_3 - /Z'^3 \ldots\ldots\ldots\ldots,$$

where a_i are constants for the whole isoelectronic series. a_1 identically equals zero by choice and therefore the lowest order perturbative correction is given by a_2 which is all we have reported in this communication. The results for the whole series is very encouraging (Table 1). For all the elements of the isoelectronic series, the zero order energy obtained through our prescription, is variational ! For He the second order energy almost coincides with the three parameter variational result of Wu [8] ! The case of H^- is even more striking. H^- has been well investigated by many authors using the variational method of which the earlier simple one parameter Kellner type [1] trial wave function leads to an energy value –0.473 which is not conclusive enough to a stable bound state. However, the better variational ansatz of the two parameter Chandrasekhar wave function [18] leads to binding at the energy value –0.514. The three parameter variational result of Wu [8] leads to an energy value –0.521. Our method yields a better value at –0.524. Our success with H^- for which $1/Z'$ is greater than unity is a very interesting feature of our method. This is presumably due to the dominant constant contribution a_2 to the energy In Table 1, we compare our result with the exact value reported by Freund *et al* [17] employing a 230 term trial wave function. They reported variational energy accurate to within one part in 10^{23} which has far exceeded the limits of accuracy in any experimental measurement. We conclude in passing that our calculation is simple, and yet yields the result comparable with those of the multiparameter cumbersome calculation reported by several workers.

Unlike in the variational ansatz, where correlation is explicitly built in the trial wavefunction, here the correlation effects come through the various orders of perturbation

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